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Glass foams from cathode ray tubes

Ana R. Barbosa[a]*, Andreia A. S. Lopes[a], Regina C. C. Monteiro[a] and F. Castro[b]

[a]*Department of Materials Science, CENIMAT/I3N, Faculty of Sciences and Technology, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*

[b]*Department of Mechanical Engineering, University of Minho, 4800-058 Guimarães, Portugal*

Abstract

Cathode Ray Tube (CRT) waste glasses produced from dismantling TV sets were used to prepare glass foams by a simple and economic processing route, consisting of a direct sintering process of mixtures of waste glass powder (CRT) with a foaming agent (fly ashes, FA, from burning of coal). The foaming process was dependent on the composition of the mixture of raw materials (with 2 and 5 wt% FA additions) and on the sintering temperature (in the range 500 to 800 ºC). During the sintering process an oxidative reaction occurred with the release of CO2 from the foaming agent. The results allowed to study the influence of the processing conditions on the evolution of the porosity and of the pore size distribution and to analyse a relationship between these microstructural characteristics and the compressive strength of the developed materials. The objective is to produce resistant glass foams with good thermal and acoustic insulation properties that can be used as building materials. The structural glass foams produced in the present study, from the starting materials CRT and FA, can be considered as "green" alternative foams, being obtained by the recycling of two different types of wastes.

Keywords: Glass foams; Cathode Ray Tube (CRT); Fly Ashes.

1. Introduction

In Europe, industrial activities related to the dismantling of end of life electronic goods have been developed in order to avoid waste landfill disposal. Such dismantling produces Cathode Ray Tubes (CRT) as sorted material. CRT represent about two thirds of the weight of a television or of a computer monitor and are composed of 85% glass [1]. Recycling techniques for metals, plastics and for different electronic components already exist, while the utilization of CRT glasses is still quite problematical due to the fact that each type of CRT has different chemical composition, which includes hazardous and heavy elements such as lead, cadmium or mercury [1]. Different approaches to the recycling of CRT have been developed [1-6].Foam glass has already been produced from CRT waste glass and it has been reported that there are no known technical barriers to use waste CRT glass [3]. The obtained product would be marketed as loose fill aggregate replacement for concrete products. According to some authors, it should be technically feasible to include up to 20% CRT panel in foam glass formulation [3]. So far, the results obtained on the recycling of CRT were promising, but they are not yet transferred into a market reality [3].

Waste glass recycling in glass foams allows energy

* Corresponding author.

E-mail address: arj.barbosa@campus.fct.unl.pt

saving, typically due to the low temperature of viscous flow, as well as to the reduction on the need for natural raw materials. The properties of finished foamed glass products depend strongly on the type and quantity of added foaming agents, on the initial glass particle size and on the firing schedule. Commercial glass foams present low density, typically in the range of 0.1–1.2 g cm^{-3} and high porosity, typically in the range of 45–85% [7]. They also combine other properties, such as stiffness, compression and fire resistance and chemical inertia, as well as low transport costs. Owing to these characteristics, glass foams can be used for thermal and acoustic insulation, as a valid alternative to polymeric foams, currently employed.

This study is focused on the physical and mechanical properties of glass foams produced exclusively from wastes, CRT glass as the base material and coal fly ashes as the foaming agent. The use of fly ashes represents an important economic advantage, since the costs of glass foams are also affected by the type of the used foaming agent [8]. In the world, the production of fly ashes from coal fire power plant is estimated to be approximately 500 000 000 ton per year [9]. The amounts of the generated waste and the environmental impact of its disposal have enhanced the search for alternative recycling solutions (both in an improved economic and environmental perspectives). Typically, fly ashes are potentially a valuable material for civil engineering applications such as road construction, embankments, construction materials, geo-polymer applications and cement production [10]. Taking into account the presence of some unburnt coal in fly ashes, and the oxidative reaction of carbon with CO_2 release at temperatures above 700 ºC, this type of wastes became a potential source to be used as foaming agent in the production of glass foams.

In the present work, the physical, thermal and chemical characteristics (density, particle size, glass transition temperature and chemical composition) of CRT waste glass coming from an asset recovery service were investigated and glass-foams based on CRT with added FA were prepared by a sintering route. The physical and mechanical properties of the produced materials were investigated and discussed in terms of the experimental processing parameters, being compared with those of commercial glass-foams products.

2. Materials and methods

The as-received CRT glass has been already crushed and the size of most fragments was 1-2 mm. It was further milled with distilled water using an agate ball mill (Fritsch, Pulverizette). After drying, the powder was sieved to obtain a glass powder fraction with a particle size smaller than 65 μm that was used in all experiments. Fly ashes from coal-fired power plant (FA), used as foaming agent, were received as very fine powders, and exhibited a particle size below 65 μm. Particle size distribution of the stating powders was determined by a laser diffraction analyzer (Malvern, Mastersizer Hydro 2000MU). The powder density (ρ_{as}) was measured by a helium pycnometer (Micrometrics, Accupyc 1330). The chemical composition was analysed by X-ray fluorescence (XRF spectrometer, PANalytical, Axios). The composition in terms of oxides (wt%) was as follows for CRT waste glass (i): 46 SiO_2, 27 PbO, 8 K_2O, 46 Na_2O, 6 CaO, 2.8 Al_2O_3, 2.8 BaO, 1.6 SrO, 1.5 MgO and some minor oxides, the content of each one being less than 0.5 wt%; and for FA (ii): 44 SiO2, 19 Al2O3, 6 Fe_2O_3, 1.7 K_2O, other minor oxides present as less than 1 wt%, and a weight loss on ignition of about 16 wt% due to the presence of unburnt coal. The thermal behaviour during heating of both starting waste powders was studied by differential thermal analysis (DTA) and thermogravimetry (TG) using a thermal analyser equipment (Linseis, STA PT1600).

The CRT glass powder was mixed with FA and mechanically mixed for 3h (Turbula WAB, T2F). The weight proportions of foaming agent were 2 and 5 %. The powders were uniaxial pressed using a compressive stress of 80 MPa and the resulting parallelepiped compacts (5mm x 5mm x 35 mm) were heat-treated in an electric muffle furnace during 30 min at different temperatures, in the range 600 to 800 ºC, using a heating rate of 5 ºC/min. For comparison, samples made totally of CRT glass powder were prepared in a similar way.

Apparent density (ρ_a) of the sintered samples was calculated according to the standard procedure (ASTM C20-83, vol.15.01, 1985), using the dry weight of the sample and the suspended weight in water. The total porosity (P) of each sintered specimen has been calculated from the apparent (ρ_a) and absolute (ρ_{as}) densities according to Eq. 1.

$$P\ (\%) = (1 - \rho_a/\rho_{as}) \times 100 \qquad (1)$$

Compressive strength tests were performed in sintered specimens with average dimension of 0.5mm x 0.5mm x 10mm, using a universal testing machine (Shimadzu

AG) with a load cell of 50 kN and a crosshead speed of 0.5 mm/min. At least five samples for a given composition and sintering treatment were tested and the average value was determined.
Microstructural observations of sintered samples were performed by optical microscopy (Leica DMI 5000M), and stereological analysis was performed using ImageJ software to evaluate the mean pore size and pore size distribution.

3. Results and discussion

The thermal behaviour of the starting powders at different temperatures is shown in Figure 1. DTA and TG curves obtained for CRT waste glass (Fig. 1a) are typical of a vitreous material. From DTA curve, a glass transition temperature (Tg) value of about 550 ºC was determined, and a sharp exothermic effect was observed at around 700 ºC, which may be associated to a structural transformation. The TG curve obtained for CRT glass (Fig.1a) did not reveal any weight loss during heating, as it is expected for a glass.

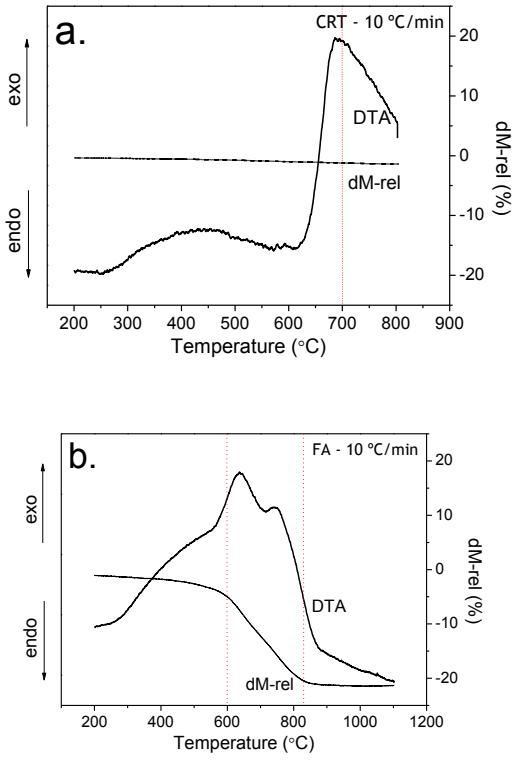

Fig. 1. DTA and TG curves for a) CRT glass powder and for b) fly ash.

DTA results for FA (Fig. 1b) show an exothermic effect above 600 ºC and up to 850 ºC, which is associated to the occurrence of an appreciable weight loss (about 15 wt%) in this temperature range as shown by TG curve (Fig. 1b). The residual non-burnt coal present in FA reacts during heating according to the exothermic reaction C (s) + O_2 (g) → CO_2 (g), and considering the TG results presented in Fig. 1b, the oxidation of the carbon begins at about 500 ºC and finishes at about 850 ºC. The foaming process involves the release of gases in a sintered glass body. When the porous structure is already closed the gases can be confined in the glass matrix. The sintering temperatures (in the range 600-800 ºC) have been selected taking into account the glass transition temperature of the CRT glass (about 550 ºC) and the temperatures needed for the occurrence of the above reaction. During sintering, coal fly ash will act as an oxidative foaming agent. The influence of sintering temperature and of the amount of foaming agent on the apparent density (ρ_a) and total porosity (P) of the produced glass foams is shown in Figure 2.

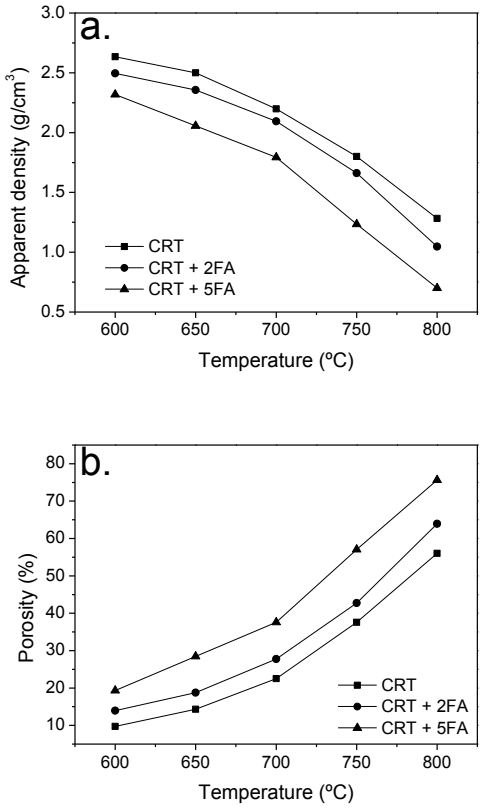

Fig. 2. a) Apparent density and b) total porosity versus sintering temperature for CRT waste-based glass foams with different amounts of added foaming agent (coal fly ash).

A linear behavior of apparent density and total porosity is observed for all treatment temperatures and foaming content. CRT glass free-foaming has no foam properties due to its apparent density being above to the maximum required. And the porosity minimal values are just achieved for 800 ºC, as shown in Figure 2b. According to the expectations, the foaming agent addition provides the foaming properties. The required values are observed for 750 and 800 ºC. The best results are for CRT-5FA with 57 and 76 % of porosity and 1.2 and 0.7 g/cm^3 of apparent density, for the treatment temperatures of 750 ºC and 800 ºC, respectively.

The mechanical resistance of the various samples was evaluated, and the compression mechanical strength values obtained for CRT-FA samples sintered under specific experimental conditions (sintering temperature and foaming agent content) are presented in Figure 3.

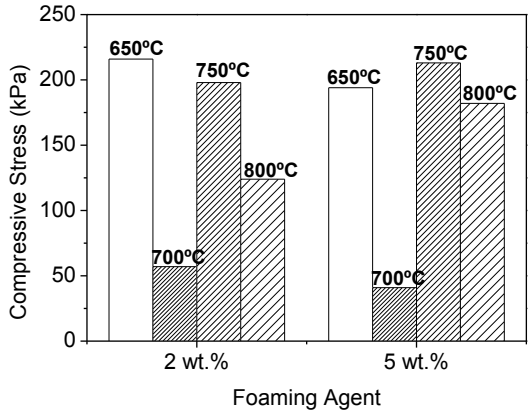

Fig. 3. Compressive strength of CRT glass-FA samples sintered at 650, 700 and 800 ºC.

The compressive strength values obtained for samples sintered at 650 ºC are much higher than those obtained for samples sintered at 700 ºC, because after sintering at 700 ºC the samples present a lower density and therefore a higher porosity (as illustrated in Fig. 2). Such decrease in strength is associated to the production of gas inside the samples, which is occluded inside the closed pores. When the oxidative reaction starts (close to 600 ºC), the glass is already in a viscous state because this heat-treatment temperature is higher than Tg for CRT glass (550 ºC). The viscosity of the glass will decrease with the increase of temperature facilitating the expansion of the sample due to gas pressure and consequently the increase of the pores size. In agreement with this phenomena, it should be expected a decrease in the compressive strength values with the increase of the sintering temperature. However, for samples sintered at 750 ºC, although exhibiting higher porosity values than at 700 ºC (see Fig. 2), much higher strength values were obtained (see Fig. 3). For both compositions, similar behaviour with increasing temperature can be observed.

X-ray diffraction analysis (not shown) performed in samples sintered at the different temperatures revealed only the presence of an amorphous (vitreous) phase, therefore the increase in compressive strength was not associated to a phase transformation (glass crystallization).

Investigations on the glass foams microstructures were performed in order to analyse porosity evolution and pore size distribution. Figure 4 presents a photograph of some CRT-5FA samples sintered at various temperatures, which have been cutted with a diamond saw in order to show the internal surfaces. Clear evidence of pore size growth with sintering temperature is given by this macroscopic observation.

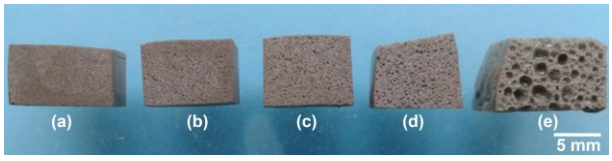

Fig. 4. Foam glass structures produced with 5 wt% addition of FA and sintered at (a) 600 ºC; (b) 650 ºC; (c) 700 ºC; (d) 750 ºC; (e) 800 ºC.

Figure 5 presents the optical micrographs of glass foam samples obtained with 5 wt% FA addition after sintering at 700ºC and 750ºC. It is observed that the increase in heat treatment temperature resulted in a higher and much more heterogeneous porosity. By stereological analysis of the microstructures of CRT-5FA samples sintered at 650, 700 and 750 ºC, it was evaluated a mean pore size of 70, 79 and 145 µm, respectively, and a pore size distribution as presented in Figure 6. It is observed that CRT-5FA glass foam samples obtained at 750 ºC exhibit a more heterogeneous pore size distribution than samples obtained at 650 and 700 ºC, which show a comparable pore size distribution, although the total porosity at 700 ºC is higher than at 650ºC.

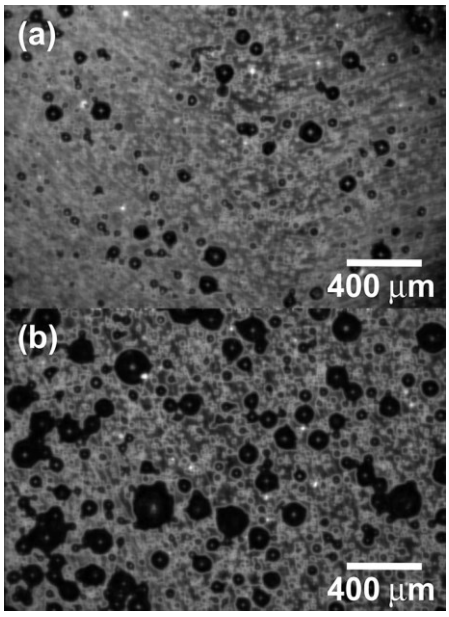

Fig.5. Optical micrographs of samples foamed with 5 wt% FA addition and sintered at (a) 700 ºC and (b) 750 ºC. (Bright field; magnification of 50x).

In samples sintered at 650 and 700 ºC, all the pores have a size below 200 µm, 40-45 % of the number of pores with a size below 50 µm and about 40% with a size between 50 and 100 µm. At 750 ºC, about 40 % of the pores have a size lower than 100 µm, the percentage of pores with a size between 100 and 200 µm is about 40% and the size of the remaining pores is in the range 200-400 µm. In spite of the higher total porosity observed in samples sintered at 750 ºC relatively to samples sintered at 700 ºC, the occurrence of such heterogeneous pore size distribution appears to be associated to the increase in compressive strength observed for samples sintered at 750 ºC.

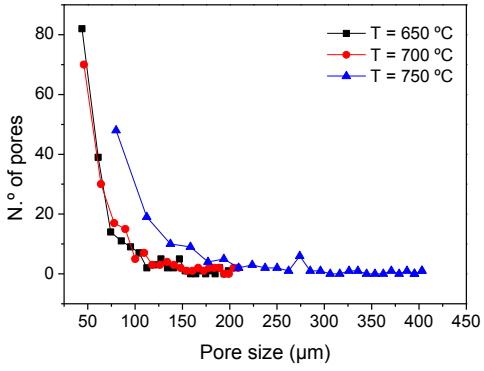

Fig.6. Pore size distribution of CRT–5FA glass foams sintered at 650 ºC, 700ºC and 750 ºC.

4. Conclusions

It is worth to note that the glass foams obtained in this work, comparable to opening to possible environmentally sustainable technological applications [7].

The obtained results proved that fly ash, a by-product from coal burning in power plants, is a promising alternative to conventional additives for glass foam production, replacing commercial foaming additives. This implies an advantage in both saving of natural resources and reusing of waste. The usage of CRT waste to produce glass foams leads to additional benefits, since it is a recycling methodology for this inorganic solid waste, which presents characteristic sintering temperatures compatible with foaming by oxidation of coal fly ashes. The foaming process occurs at temperatures (650–800 ºC) well below those employed for commercial glass foams produced from oxidation of carbonaceous-containing compounds added to common soda-lime glass.

The foaming temperature of 750 ºC led to foams with a heterogeneous pore size distribution that was associated to a good compressive strength (higher than 200 kPa) having an apparent density about of 1.2 g/cm^3 and a porosity of 57 % , comparable to those of commercial foams. Therefore, glass foams obtained in this work are potential cellular materials for environmentally sustainable technological applications.

Acknowledgements

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